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**No. 57: SOME EXPERIMENTS ON RESIDUAL IONIZATION,  
BY K. H. KINGDON**

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*Some Experiments on Residual Ionization.*

By K. H. KINGDON, M.A., *University of Toronto*.\*

[Plate X.]

*I. Residual Ionization in Acetylene.*

**INTRODUCTION.**—If dry air be enclosed in a clean zinc vessel and removed from the neighbourhood of all ordinary ionizing agents, it is found, on measuring the conductivity of the gas, that ions are being produced in it at the rate of about 8·7 per c.c. per second. The production of these ions is called natural ionization. If, however, the zinc vessel be surrounded by a water-screen the natural ionization is found to decrease; and if the measurements be made over a considerable body of water, such as the ocean or the great lakes of America, the ionization in air is found to fall to a definite minimum of about 4·4 ions per c.c. per second, which we may call the residual ionization. The difference between these two rates of ionization has been shown to be due to a penetrating radiation from the earth's surface, which can be cut off by a screen of water if sufficient thickness be used. The possible components of the residual ionization appear to be:—(1) a radioactive impurity in the gas, (2) a radioactive impurity in the walls of the ionization-chamber, (3) ionization by the collisions of thermal agitation. In an effort to determine to which of these sources residual ionization should be attributed, McLennan and Treleaven† measured the residual ionization in several gases, the results obtained being as follows:—

| Gas.                 | No. of ions per c.c. per second. |
|----------------------|----------------------------------|
| Carbon Dioxide ..... | 4·83                             |
| Hydrogen .....       | 1·11                             |
| Ethylene .....       | 6·32                             |
| Nitrous Oxide.....   | 5·02                             |
| Acetylene .....      | 27·00                            |

It will be noticed that in the above list the residual ionization in acetylene is very much higher than in any of the

\* Communicated by Professor J. C. McLennan, F.R.S.

† J. C. McLennan and C. L. Treleaven, *Phil. Mag.* xxx. p. 415 (1915).

other gases, a fact which certainly cannot be accounted for on the ground of its density. The present investigation was therefore undertaken to see whether this large ionization could be traced to either of the sources (1) or (3) above. As a result, it has been found that in acetylene made from calcium carbide there is present a slight trace of radium emanation, and this it has been shown accounts for the high residual ionization in the gas.

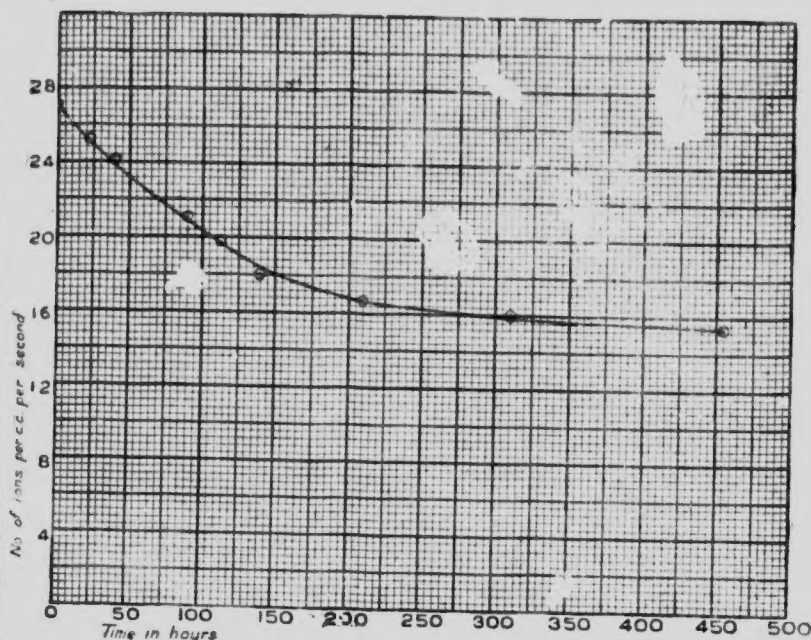
*Experiments.*—The gas used at first in the experiments with acetylene was taken from a commercial Prest-o-Lite tank. The ionization-chamber was made of zinc because it has been shown that this metal contains smaller traces of radioactive impurities than any other. The external dimensions of the chamber were:—diameter 11.6 cm., length 22.8 cm., and its volume was 2167 c.c. The thickness of the walls was about 3 mm. The chamber was carefully scoured with emery, and washed with dilute hydrochloric acid and water, to remove radioactive deposits. During all the course of the work the chamber was absolutely air-tight. It was provided with a zinc electrode which was connected to a sensitive electrometer in the usual manner. The wall of the chamber was kept at a potential of 240 volts, which ensured that all the currents measured were saturation currents.

The ionization-chamber was filled with acetylene which had been carefully dried and freed from dust, and the number of ions made per c.c. per second was found to be about 20. As this number was considerably less than that previously found by McLennan and Treleaven, the zinc Wolf electrometer (Pl. X. fig. 1) used by them was filled with acetylene from the Prest-o-Lite tank, and the number of ions made per c.c. per second was found to be only 12. The difference between this number and that found with the zinc ionization-chamber was probably due to a radioactive impurity in the walls of the latter. It was thought that the low value of the ionization was due to the commercial acetylene not being pure, and to test this some acetylene was made in the laboratory from calcium carbide, and both the Wolf electrometer and the zinc ionization-chamber were filled with it. The number of ions made per c.c. per second ( $n$ ) was measured at intervals during a period of about 19 days. The following set of readings was obtained with the Wolf electrometer, and a similar set with the zinc ionization-chamber.

| T (hrs.). | n.   |
|-----------|------|
| 0         | 27.0 |
| 22        | 25.2 |
| 41        | 24.1 |
| 78        | 21.1 |
| 113       | 19.8 |
| 139       | 18.0 |
| 209       | 16.7 |
| 310       | 16.0 |
| 454       | 15.4 |

A curve plotted from these readings is shown in fig. 2.

Fig. 2.

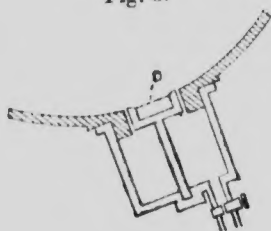


The decrease in the ionization clearly indicates the presence of some radioactive impurity in the gas. From the shape of the curve it may be estimated that the number of ions made per c.c. per second would finally fall to about 15. From this the number of ions per c.c. per second initially due to the radioactive impurity was about 12. As this number of ions had decreased to 6, or to one half, in about 90 hours (3.8 days), it may be concluded that the impurity was radium emanation. In the gas from the Pres-Lite tank this

emanation had had ample time to decay, and so the number of ions made per c.c. per second was quite low.

To make certain of the source of the emanation the calcium carbide was tested for radioactivity in the following manner. A metal cap, fig. 3, was made which could be screwed on

Fig. 3.



in place of the drying-tube of the Wolff electrometer. A small brass cup, which was to contain the carbide, was supported on a rod screwed into the end of the cap. The figure shows the cap in place, the top of the cup being flush with the wall of the electrometer. The following measurements were made. The cup was put in place, and the electrometer filled with fresh, dry air. The number of ions made per c.c. per second,  $n$ , was then measured. The cup was removed, filled with powdered carbide, and the carbide was covered with aluminium foil  $\cdot 0003$  cm. thick. The cup was then replaced in the electrometer, and the number of ions made per c.c. per second again measured. The next day two more measurements of the ionization were made, the first with both brass cup and carbide in place, and the second with them both removed. The air in the electrometer was the same as that used on the first day, and had probably received slight traces of radium emanation from being in contact with the carbide. Hence the values of  $n$  obtained on the second day are considerably greater than those obtained on the first day. However, the difference between the two readings taken on either day, which is the important thing here, is almost the same for both days.

| First day.                   | $n$ . | Second day.                  | $n$ . |
|------------------------------|-------|------------------------------|-------|
| Brass cup in place .....     | 8.7   | Carbide and cup in place ... | 12.2  |
| Carbide and cup in place ... | 10.6  | Both removed .....           | 10.4  |
| Difference .....             | 1.9   | Difference .....             | 1.8   |



These figures clearly indicate that the carbide was slightly radioactive. Any trace of radium emanation present would make itself very apparent in the gas generated from the carbide, and it is to the emanation that the high value of the residual ionization previously obtained was due.

## II. *On the possibility of a Portion of the Residual Ionization in Gases being due to the Collisions of Thermal Agitation.*

*Introduction.*—In the first part of this paper the three possible components of the residual ionization in gases were stated to be:—(1) a radioactive impurity in the gas, (2) a radioactive impurity in the walls of the ionization-chamber, (3) ionization by the collisions of thermal agitation. Now, for the gases air, carbon dioxide, hydrogen, and nitrous oxide, McLennan and Treleaven \* have shown that if a clean zinc ionization-chamber is used, and if the gases are properly dried and filtered before admitting them to the chamber, uniform and reproducible values of the residual ionization are obtained for each gas. Hence it does not seem probable that the residual ionization is in general due to the presence of traces of radioactive emanation in the gas. The part played by the second of the above-mentioned components has been quite fully investigated. Recently McLennan and Murray † have shown that by constructing the ionization-chamber of ice, it is possible to obtain a very low value for the residual ionization in air. Their experiments show the great effect of radioactive impurities in the walls of the chamber on the ionization, for with one ice-chamber the number of ions made per c.c. per second was 2.6, while with another the number was 5.5. Although from these experiments it appears possible that the residual ionization, in air at least, may be due entirely to radioactive impurities in the walls of the ionization-chamber, yet it seemed worth while to make some experiments to test for the presence of ionization due to the collisions of thermal agitation. The method was to vary the temperature or the density of the gas in the ionization-chamber, and from the resulting changes in the ionization to see if it was possible to detect the presence of any ionization produced by the collisions of thermal agitation. The results of the experiments in which the density of the gas was varied show that only a part of the residual ionization can be due to the collisions of thermal agitation. The results of the experiments in which the temperature of the gas was varied give

\* *Loc. cit.*

† J. C. McLennan and H. G. Murray, *Phil. Mag.* xxx. Sept. 1915.

indications of a small number of ions per c.c. per second produced by the collisions of thermal agitation, but more refined experiments are required to confirm this point. In addition a formula has been derived for the number of thermal collisions in a gas per c.c. per second producing ionization which agrees with the experimental results if the number of such collisions is small.

*Theory.*—The question of ionization by the collisions of thermal agitation has been investigated theoretically by Langevin and Rey\*. In this paper the authors obtained an expression for the number of collisions in a gas per c.c. per second for which the relative velocity of the colliding molecules normal to the sphere of shock was greater than an arbitrary standard. If we denote the number of these "effective" collisions by  $K$ , then

$$K = \nu e^{-\frac{1}{2} h m v^2},$$

where  $\nu$  = total number of collisions per c.c. per second,

$$h = \frac{3}{4\epsilon T}, \text{ and } \epsilon = 2.02 \times 10^{-16},$$

$v$  = arbitrary minimum velocity.

According to this formula  $K$  would vary very rapidly with the temperature, a prediction which is contradicted by experiment.

Exception was taken to Langevin's work by Wolfke†, who suggested that the potent factor in producing ionization at the collision of two molecules was not their relative velocity normal to the sphere of shock, but rather their relative velocity tangential to it. Indeed he suggested that the normal component would rather prevent ionization by pushing the electron further into the atom, although it is difficult to judge of the value of this suggestion on account of the very conjectural nature of our knowledge of the mechanism of an atom. However, on this ground Wolfke suggested that the number of effective collisions would depend on the relative velocity of the molecules normal to the sphere of collision being less than a certain value,  $v$ . The formula obtained for the number of effective shocks is

$$\nu(1 - e^{-\frac{1}{2} h m v^2}),$$

where the symbols have the same meaning as before. From this Wolfke calculated that if the collisions in air produce

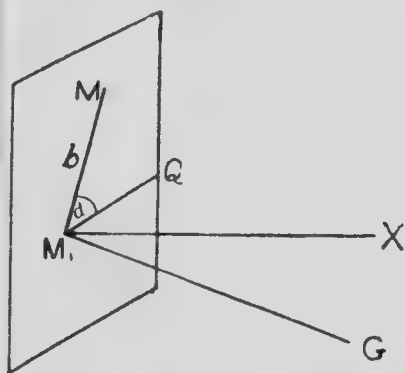
\* Langevin and Rey, *Le Radium*, x. p. 142 (1913).

† Wolfke, *Le Radium*, x. p. 265 (1913).

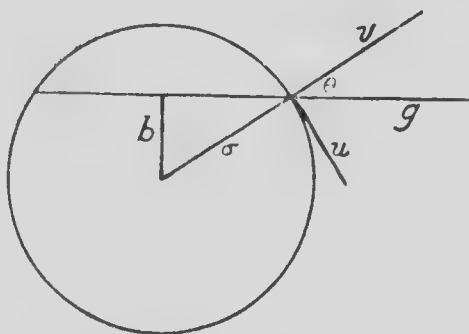
The expression for the total number of collisions per c.c. per second is obtained by Boltzmann as follows. We assume the presence of two kinds of molecules of masses  $m$  and  $m_1$  respectively;  $n$  and  $n_1$  are the numbers of each kind per c.c.;  $d\omega$  and  $d\omega_1$  represent the products of the velocity components for each kind; and  $f, f_1$  represent for the two kinds of molecules the values of the function

$$n \sqrt{\frac{h^3 m^3}{\pi^3}} e^{-kmc^2}.$$

Fig. 4 a.



**Fig. 4 b.**


$$v = \int f f_1 g b d\omega d\omega_1 db da;$$

or integrating for  $a$  from 0 to  $2\pi$ ,

$$\nu = 2\pi \int b db \int g_1 f_1 d\omega d\omega_1,$$

Langevin has carried out four of the remaining integrations in such a way as to obtain the result

$$v = \frac{2\pi^3 k^2}{hm} \sqrt{\frac{\pi}{2hm}} \int_0^\sigma b db \int_0^\pi g^3 e^{-\frac{1}{2}hmg^2} d\eta,$$

where  $\sigma$  is the radius of the sphere of action of the molecule and

$$k = n \sqrt{\frac{h^3 m^3}{\pi^3}}.$$

If now we let  $\theta$  (fig. 4 *b*) be the angle between  $g$  and the normal to the sphere of action, then  $v$  the velocity normal to this sphere is equal to  $g \cos \theta$  and  $b = \sigma \sin \theta$ . Making these substitutions in the above integral, we obtain for the total number of collisions per c.c. per second for which the relative velocity normal to the sphere of action is less than a certain  $v$ ,

$$\begin{aligned} L &= \frac{2\pi^3 k^2 \sigma^2}{hm} \sqrt{\frac{\pi}{2hm}} \int_0^v v^3 dv \int_0^\pi \frac{\sin \theta}{\cos^3 \theta} e^{-\frac{hmv^2}{2\cos^2 \theta}} d\theta \\ &= \frac{2\pi^3 k^2 \sigma^2}{h^2 m^2} \sqrt{\frac{\pi}{2hm}} \int_0^v v e^{-\frac{1}{2}hmv^2} dv \\ &= \frac{2\pi^3 k^2 \sigma^2}{h^3 m^3} \sqrt{\frac{\pi}{2hm}} (1 - e^{-\frac{1}{2}hmv^2}) \\ &= n^2 \sigma^2 \sqrt{\frac{2\pi}{hm}} (1 - e^{-\frac{1}{2}hmv^2}). \end{aligned}$$

To obtain the number of collisions per c.c. per second for which the relative velocity tangential to the sphere of collision is greater than a certain  $u$ , put  $u = g \sin \theta$ , and  $b = \sigma \sin \theta$  in the expression for  $v$  above. Then the number of such collisions is

$$\begin{aligned} M &= \frac{2\pi^3 k^2 \sigma^2}{hm} \sqrt{\frac{\pi}{2hm}} \int_u^\infty u^3 du \int_0^\pi \frac{\cos \theta}{\sin^3 \theta} e^{-\frac{hmu^2}{2\sin^2 \theta}} d\theta \\ &= \frac{2\pi^3 k^2 \sigma^2}{h^2 m^2} \sqrt{\frac{\pi}{2hm}} \int_u^\infty u e^{-\frac{1}{2}hmu^2} du \\ &= \frac{2\pi^3 k^2 \sigma^2}{h^3 m^3} \sqrt{\frac{\pi}{2hm}} e^{-\frac{1}{2}hmu^2} \\ &= m^2 \sigma^2 \sqrt{\frac{2\pi}{hm}} e^{-\frac{1}{2}hmu^2}. \end{aligned}$$

Hence the probability that for any collision the relative velocity of the molecules normal to the sphere of action shall be less than  $v$  is  $(1 - e^{-\frac{1}{2}hmv^2})$ , since  $n^2\sigma^2\sqrt{\frac{2\pi}{hm}}$  is the total number of collisions per c.c. per second. Similarly the probability that the relative velocity tangential to the sphere of action shall be greater than  $u$  is  $e^{-\frac{1}{2}hmu^2}$ . Therefore the probability that both these conditions are fulfilled for a particular molecule is

$$e^{-\frac{1}{2}hmu^2}(1 - e^{-\frac{1}{2}hmv^2}),$$

and the number of such collisions per c.c. per second will be

$$N = n^2\sigma^2\sqrt{\frac{2\pi}{hm}} e^{-\frac{1}{2}hmu^2}(1 - e^{-\frac{1}{2}hmv^2}).$$

*Experiments.*—The only experimental work which has been done on this subject is by Patterson \*, and by Devik †. In Patterson's work the gas was contained in an iron cylinder, and as iron usually contains some radioactive impurity, the number of ions generated per c.c. per second was quite large ( $n=61$ ). He failed to detect any effect of temperature on the ionization up to  $400^\circ\text{C}$ ., but it is possible that the effect might have been masked by the largeness of the currents measured. Also, as the air in the receiver was always at atmospheric pressure, its density would decrease as the temperature was raised; this decrease in density would decrease the ionization current due to the earth's penetrating radiation and also that due to a radiation of the  $\beta$  or  $\gamma$  type coming from impurities in the walls of the chamber, both of which form part of the total current measured.

In Devik's experiments the gas was momentarily heated by an adiabatic compression, and the ionization measured at the moment of greatest compression. The only gas which showed any signs of ionization caused by the high temperature (estimated at  $900^\circ\text{C}$ .) was antimony hydride.

In view of the methods of the above experiments, it was thought worth while to carry out another investigation in which the following conditions should be satisfied:—(1) the ionization-chamber should be airtight; (2) the residual ionization should be as low as possible so that any change would make itself more apparent; (3) the temperature should be kept constant during the time of each reading. Unfortunately, in order to fulfil these requirements the range of

\* Patterson, *Phil. Mag.* vi. p. 231 (1903).

† Devik, *Sitz. d. Heil. Akad. Wiss.* xxiv. (1914).

temperature had to be reduced considerably. The zinc ionization-chamber previously described was used. It was covered with thin asbestos, then wound with nichrome resistance-wire, and packed in magnesia. By passing currents up to 1.5 amperes through this wire, the chamber could be maintained at any temperature between  $10^{\circ}$  and  $100^{\circ}$  C. for as long a time as desired. The chamber was absolutely airtight, the wax joints around the electrode and guard-ring being kept cool with a water-jacket. The temperatures were calculated from the changes in pressure.

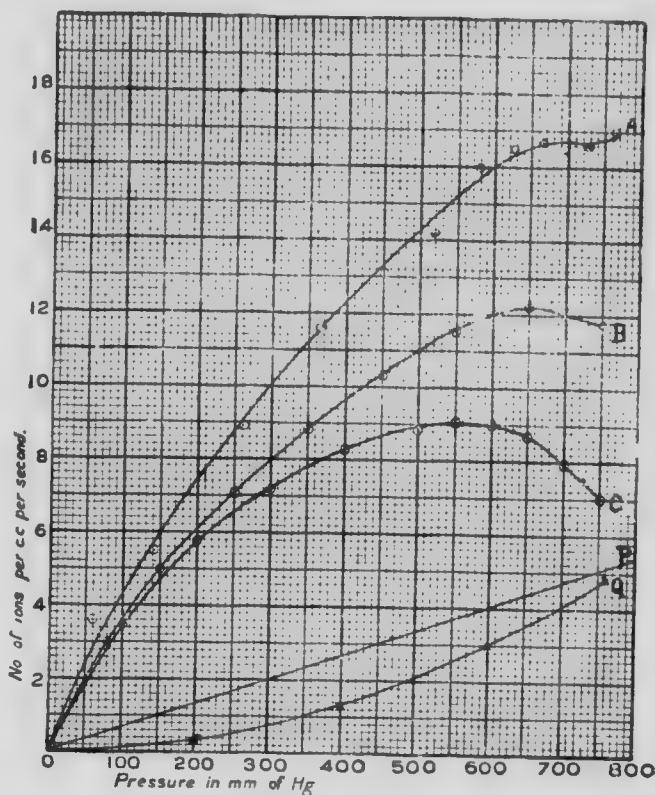
*Variation of Ionization with Pressure.*—The gases used were carbon dioxide, acetylene, and hydrogen. Several sets of readings were taken with each of these gases at room temperature to show the connexion between ionization and pressure. The readings and curve (fig. 5) shown were obtained with carbon dioxide, and are typical of the others. The ionization shows a slight maximum at 650 mm. pressure, due presumably to a soft radiation from the walls of the chamber.

| $p$ (mm.). | $n$ . |
|------------|-------|
| 764        | 17.0  |
| 726        | 16.6  |
| 667        | 16.7  |
| 626        | 16.5  |
| 579        | 16.0  |
| 519        | 14.2  |
| 450        | 13.1  |
| 386        | 11.6  |
| 262        | 8.9   |
| 141        | 5.5   |
| 60         | 3.6   |

We may proceed as follows to see whether this curve gives any indication of the presence of ionization by collision. The possible components of the ionization are—(1) the ionization due to the earth's penetrating radiation, which from the experiments of McLennan and Treleaven will be about 5.1 ions per c.c. per second at 760 mm. pressure; (2) that due to a possible ionization by thermal collisions, which from the same experiments cannot be more than about 4.8 ions per c.c. per second at 760 mm. pressure; (3) that due to any radioactive impurity in the walls of the receiver. Now component (1) will vary directly as the pressure, and may be

represented by the straight line OP in the figure. If we diminish the ordinates of OA by the corresponding ordinates of OP we obtain the curve OB, which is the ionization-pressure curve for the remaining components.

Fig. 5.



Again, on the above theory of ionization by thermal collisions, the number of ions produced per c.c. per second varies as the square of the number of molecules per c.c., and therefore as the square of the pressure. Hence the pressure-ionization curve for this component may be represented by the curve OQ. By diminishing the ordinates of OB by the corresponding ordinates of OQ, the curve OC is obtained, which is the pressure-ionization curve for the radiation from the walls of the chamber. This curve shows a very pronounced maximum at a pressure of 550 mm.; and it is evident that if it is possible for a curve such as OC to represent correctly the pressure-ionization curve for a soft radiation,

then it is possible that about 5 ions per c.c. per second are produced in the gas by the collisions of thermal agitation. Now it is a well-known fact that when a radiation produces ions in a gas, the total number of ions made is the same so long as the radiation is totally absorbed in the gas; also the effect of recombination will be least, and therefore the current will be greatest, when the gas is at such a pressure as just to absorb the rays. Hence it is possible that for a certain range of pressures the current will increase as the pressure decreases, on account of the effects of recombination. The conditions of this experiment are particularly favourable for a large recombination effect, since the direction of the rays is perpendicular to the direction of the electric field, and also since carbon dioxide is a heavy gas. Yet in spite of these arguments it seems improbable that the effects of recombination could cause a rise from 7 to 9 ions per c.c. per second, or an increase of about 33 per cent. in the current, as is the case here. These results would therefore seem to show that the residual ionization cannot be wholly due to the collisions of thermal agitation. They cannot, however, be said to exclude the possibility that a smaller number of ions than 5 p. c.c. per second may be due to these collisions.

*Variation of Ionization with Temperature.*—The gases used were carbon dioxide and acetylene, and the range of temperature was from  $18^{\circ}$  to  $100^{\circ}$  C. Great difficulty was experienced in getting reliable sets of readings; for as each set required a period of from six to eight hours, it was quite possible that the leak of the electrometer might vary during this time. As a determination of the leak required that the ionization-chamber be exhausted, and as also it was found that in order to obtain consistent readings the gas had to be allowed to stand in the chamber for some time before commencing readings, it was only possible to obtain one leak reading for each set of temperature readings. All the sets of readings, however, agree in showing that the ionization is practically unchanged from  $18^{\circ}$  to about  $80^{\circ}$  C. For temperatures from  $80^{\circ}$  to  $100^{\circ}$  some sets of readings show a very marked increase in the current, while in others this increase is very small. The two chief sources of possible error would appear to be thermo-electric currents, and the driving off of minute quantities of radioactive emanation from the walls of the ionization-chamber as its temperature was raised. These errors were guarded against by eliminating possible thermo-junctions, and by exhausting the ionization-chamber while it was heated to  $100^{\circ}$ . To test for the presence of thermo-electricity the junction of the brass electrode and the



brass connecting wire at the top of the ionization-chamber, which junction was the only one that could possibly serve as a hot junction, was heated with a small flame, the flame was removed, and the earth connexion to the quadrants of the electrometer broken, but no change could be detected in the normal ionization current flowing to the electrometer. It seems likely though that the rise in current sometimes noted at temperatures of about  $100^{\circ}$  was due to small quantities of emanation being driven off from the walls of the chamber.

It might be interesting to see if the proposed formula for  $N$  agrees at all with the results of the temperature experiments. The experiments on pressure show that the number of ions produced per c.c. per second in carbon dioxide at  $20^{\circ}$  C. and 760 mm. pressure is probably less than four. In the expression for  $N$  we have then to assign values to  $u$  and  $v$  so that the following conditions may be fulfilled:

- (1)  $N$  must be about 4 at  $20^{\circ}$  C. and 760 mm. pressure.
- (2)  $N$  must change slowly with the temperature, at least in the region of  $20^{\circ}$ .

The only physical condition suggesting itself which will fulfil the above requirement is that, for a collision to produce ionization, it must be almost perfectly tangential (this will make the total number of such collisions small), and that the arbitrary minimum tangential velocity of each of the colliding molecules must be about equal to the most probable velocity for a temperature of  $20^{\circ}$  (this ensures that  $N$  shall change slowly with the temperature in this region). Then for carbon dioxide, if we put the minimum relative tangential velocity  $u = 2\alpha = 2 \times 3.43 \times 10^4$  cm. per second, and the maximum relative normal velocity  $v = 8.97 \times 10^{-10}$  cm. per second, we find that at  $20^{\circ}$  C.,  $N = 4$ , and at  $100^{\circ}$ ,  $N = 5.1$ . That is,  $N$  changes very slowly as the temperature is raised, which is in qualitative agreement with the experimental results. A more exact application of the formula for  $N$  does not seem worth while at the present time, since, for the reasons stated above, the accuracy of the readings does not warrant it. It may, however, be of interest to note that using the above values for  $u$  and  $v$ , and making changes in  $h$ ,  $p$ , and  $\eta$  to correspond to the rise in temperature, at  $302^{\circ}$  C. the value for  $N$  is 6.4.

#### *Summary.*

- (1) It has been shown that the high residual ionization in acetylene prepared from calcium carbide is due to the presence of slight traces of radium emanation.

(2) It has been shown that only a portion of the ultimate residual ionization in gases can be due to the collisions of thermal agitation.

(3) A formula has been devised for the number of collisions per c.c. per second producing ionization which is in qualitative agreement with experimental facts.

In conclusion the author wishes to express his thanks to Professor J. C. McLennan, who suggested the problem, and whose assistance and encouragement have been most valuable.

Physical Laboratory,  
University of Toronto.  
May 8, 1916.

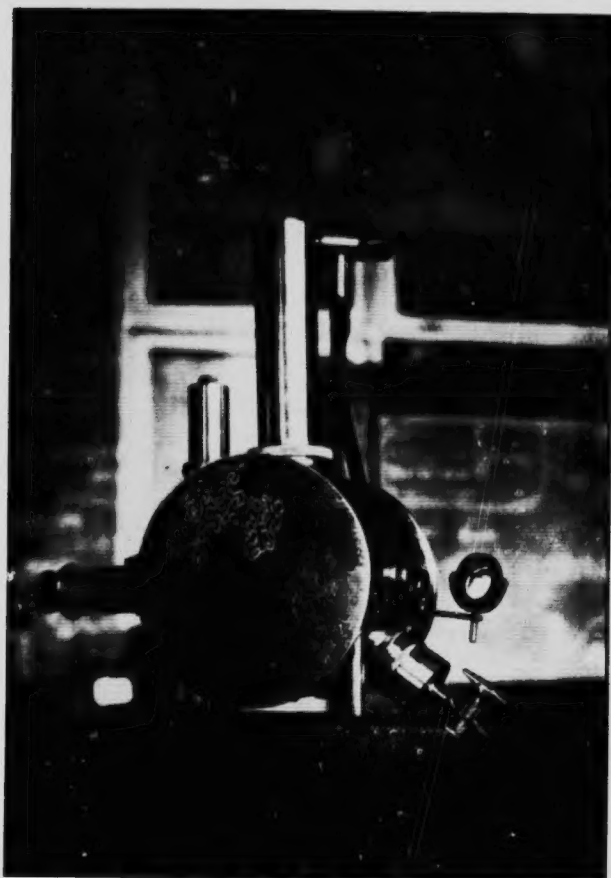


FIG. 1.

